Novel Hetero Trinuclear Complexes Triply Bridged by Carbon Disulphide; *X*-Ray Crystal Structure of The Complex $[(OC)_2(\eta^5\text{-}C_5H_5)FeC(=S)SFe(\eta^5\text{-}C_5H_5)(CO)_2W(CO)_5]$ †‡

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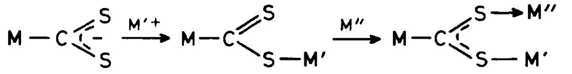
The reaction between the metallodithioester–metal complexes $[(OC)_2(cp)FeC(=S)SM(L_n)]$ $[M(L_n) = Fe(cp)(CO)_2$ or $Re(CO)_5$; cp = $\eta^5\text{-}C_5H_5]$ and $[M'(CO)_5(thf)]$ (M′ = Cr, Mo, or W) or $[Mn(cp)(CO)_2(thf)]$ (thf = tetrahydrofuran) produces in good yield stable heterotrinuclear complexes $[(OC)_2(cp)FeC(=S)SM(L_n)M'(CO)_5]$ and $[(OC)_2(cp)FeC(=S)SM(L_n)Mn(cp)(CO)_2]$ in which the CS_2 group is triply bridging. All these novel complexes have been characterized by elemental analyses, i.r., and ^1H n.m.r. spectra. The $\mu_3\text{-}CS_2$ derivatives readily decompose in solution to produce dithiocarboxylatometal complexes $[(OC)_2(cp)FeC(=S)SM(L_n)]$ $[M(L_n) = Fe(cp)(CO)$ or $Re(CO)_4]$ and $[M(CO)_6]$ (M = Cr, Mo, or W) or $[Mn(cp)(CO)_3]$, suggesting that the attachment of a metal atom to the unco-ordinated sulphur atom in the unit FeC(=S)SM does not labilize the carbon–sulphur bonds of the CS_2 molecule. The structure of the triply bridged complex $[(OC)_2(\eta^5\text{-}C_5H_5)FeC(=S)SFe(\eta^5\text{-}C_5H_5)(CO)_2W(CO)_5]$ has been determined by *X*-ray crystallography. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.647(1)$, $b = 12.145(2)$, $c = 14.795(2)$ Å, $\alpha = 82.33(1)$, $\beta = 85.73(1)$, $\gamma = 79.73(1)°$, and $Z = 2$. 3 487 Reflection intensities with $I > 3\sigma(I)$ led to R 0.024. The molecule is asymmetrical and contains a bent CS_2 unit in which the carbon and sulphur atoms are trigonally hybridized and are σ-bonded to two $Fe(\eta^5\text{-}C_5H_5)(CO)_2$ and one $W(CO)_5$ fragments. Relevant bond parameters are S–C–S 119.2(2)°, C–S 1.69(2), Fe–C 1.975(4), Fe–S 2.273(1), and W–S 2.563(1) Å.

Binuclear complexes containing a bridging CS_2 molecule have become a well known class of organometallic compounds.[1,2] Since there are no reports describing trinuclear complexes with a triply bridging carbon disulphide group,§ it was of interest to investigate their preparation and to establish the bonding mode of the bridging $\mu_3\text{-}CS_2$ as well as the properties of these novel derivatives.

A possible method of obtaining these complexes is to use a mononuclear anionic complex containing a *C*-bonded $\sigma\text{-}CS_2$ group capable of behaving as a three-electron donor dithiocarboxylate ligand, and to *S*-metallate it with a 17-electron (M'^+) and with a 16-electron (M'') metal fragment as illustrated in equation (i). The obvious candidate for such a



(i)

(A) (B) (C)

sequence is $[Fe(cp)(CO)_2(CS_2)]^-$ (cp = η^5-cyclopentadienyl)[3] since this electron-rich carbon disulphide adduct readily reacts with $[FeI(cp)(CO)_2]$ and $[ReBr(CO)_5]$ to give $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2]$[4] (1) or $[(OC)_2(cp)FeC(=S)SRe(CO)_5]$[5] (2) respectively. Moreover, the unco-ordinated thione sulphur atom in these type (B) metallodithioester-metal complexes can easily be alkylated[5,6] in agreement with its nucleophilic character.

In the present paper we describe the second step of the sequence (i), which provides a general route for the synthesis of type (C) adducts, and the crystal structure of $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2W(CO)_5]$. This structure allows the elucidation of the bonding mode of the triply bridging CS_2 which is strictly related to that of $\mu_3\text{-}CO_2$ in the very recently reported tetranuclear complex $[\{(OC)_5Re(CO_2)Re(CO)_4\}_2]$.[7]

The decomposition of the novel derivatives, which occurs without fragmentation of the carbon disulphide bridging molecule, is also reported.

Results and Discussion

Synthesis and Characterization.—The iron dithioester–metal complexes $[(OC)_2(cp)FeC(=S)SM(L_n)]$ $[M(L_n) = Fe(cp)(CO)_2$ (1)[4] or $Re(CO)_5$ (2)[5]] readily available through the reaction of $[Fe(cp)(CO)_2(CS_2)]^-$ and a suitable metal halide, react rapidly at room temperature with $[M'(CO)_5(thf)]$[8] (M′ = Cr, Mo, or W) and $[Mn(cp)(CO)_2(thf)]$[8] in tetrahydrofuran (thf) solution (Scheme 1). The thf ligand is displaced by the basic thione sulphur atom of derivatives (1) and (2), and the resulting red-brown (3a)—(3c), (5) or orange-red (4a)—(4c), (6) complexes were obtained by crystallization from CH_2Cl_2–hexane at −20 °C. All the compounds are air stable in the solid state, but decompose (see next section) in chlorinated

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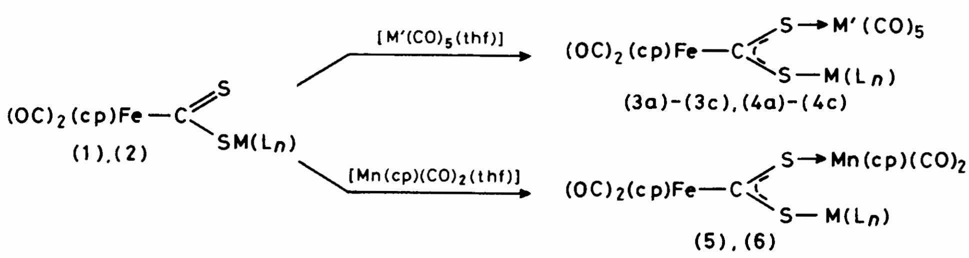
† Presented at the XV National Congress of Inorganic Chemistry, Bari, 27th September, 1982.

‡ 1,1,2,2,3,3,3,3,3-Nonacarbonyl-1,2-bis(η-cyclopentadienyl)-μ_3-[sulphido(thiocarbonyl)-*C*(Fe^1)*S*(Fe^2)*S*′(W^3)]-di-irontungsten.

§ Contemporary with this work, two of the $\mu_3\text{-}CS_2$ derivatives described herein have been reported elsewhere (H. Stolzenberg and W. P. Fehlhammer, *J. Organomet. Chem.*, 1982, **235**, C7—C9).

Supplementary data available (No. SUP 23617, 30 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme 1. $M(L_n)$ = $Fe(cp)(CO)_2$ in (1), (3), and (5), $Re(CO)_5$ in (4) and (6)

Table 1. Infrared and ^1H n.m.r. data

	Complex	I.r. (cm^{-1})		^1H N.m.r. (δ) [c]
		ν(CO) [a]	ν(CS_2) [b]	
(1)	$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2]$ [d]	2 025m, 2 013s, 1 970s	1 018s	4.31, 4.21 (4.96, 4.83)
(3a)	$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2Cr(CO)_5]$	2 055m, *2 029* (sh), *2 021*s, *1 981*s, 1 931 (sh), 1 917vs, 1 893 (sh)	948vs, 766m	4.40, 4.05 (4.95)
(3b)	$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2Mo(CO)_5]$	2 065m, *2 031* (sh), *2 023*s, *1 977*s, 1 927vs,br, 1 893 (sh)	948vs, 765m	4.43, 4.09 (4.96) [e]
(3c)	$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2W(CO)_5]$	2 061m, *2 031* (sh), *2 023*s, *1 987*s, 1 925 (sh), 1 913vs, 1 889 (sh)	942vs, 775m	4.45, 4.06 (5.01) [e]
(5)	$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2Mn(cp)(CO)_2]$	*2 029* (sh), *2 017*s, 1 *977*s, 1 907s, 1 839s	940vs, 780m	4.65, 4.50, 4.10
(2)	$[(OC)_2(cp)FeC(=S)SRe(CO)_5]$ [f]	2 125m, 2 052w, 2 019vs, 1 970s	998s, 920m	(4.88)
(4a)	$[(OC)_2(cp)FeC(=S)SRe(CO)_5Cr(CO)_5]$	*2 127*m, 2 053m, *2 025*vs, *1 975*s, 1 931 (sh), 1 917vs, 1 893 (sh)	945s, 773m	(4.99)
(4b)	$[(OC)_2(cp)FeC(=S)SRe(CO)_5Mo(CO)_5]$	*2 131*m 2 067m, *2 029*vs, *1 983*s, 1 931vs,br, 1 891 (sh)	943s, 772m	(5.01)
(4c)	$[(OC)_2(cp)FeC(=S)SRe(CO)_5W(CO)_5]$	*2 131*m, 2 063m, *2 029*vs, *1 989*s, 1 927 (sh), 1 917vs, 1 897 (sh)	945s, 778m	4.28 (5.10)
(6)	$[(OC)_2(cp)FeC(=S)SRe(CO)_5Mn(cp)(CO)_2]$	*2 125*m, *2 025*vs, *1 981*s, 1 913s, 1 847s	942s, 781m	
(7)	$[(OC)_2(cp)FeC(=S)SRe(CO)_4]$ [f]	2 093m, 2 037s, 1 995vs, 1 981 (sh), 1 933s		
(8)	$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)]$	2 033s, 1 986s, 1 940s	910s, 875m	4.20, 4.07 (4.87, 4.51)
(9)	$[(OC)_2(cp)FeC(=S)SMn(cp)(NO)]$	2 029s, 1 983s, 1 701s [g]	905s, 850m	4.50, 4.11 (4.93, 4.86)

[a] In $CHCl_3$. The absorptions due to the precursors (1) and (2) are italicized. [b] Nujol mull. [c] In p.p.m., $SiMe_4$ as internal standard. In C_6D_6 or, in parentheses, in $CDCl_3$. [d] See ref. 4. [e] Broad signal. [f] See ref. 5. [g] ν(NO).

solvents within a few hours [(4a)—(4c), (6)] or 1 d [(3a)—(3c), (5)]. Among the members of the two series of adducts the stability towards decomposition in solution is in the order $W(CO)_5 > Cr(CO)_5 > Mo(CO)_5 \geqslant Mn(cp)(CO)_2$. This trend accounts for the yields (see Experimental section) of the S-addition products. In addition, it is noteworthy that, under the preparative conditions, the reactions in Scheme 1 occur without subsequent desulphurization, suggesting that the attachment of a metal atom to the unco-ordinated sulphur atom in the unit Fe–C(=S)SM does not labilize the carbon–sulphur bonds of the CS_2 molecule.

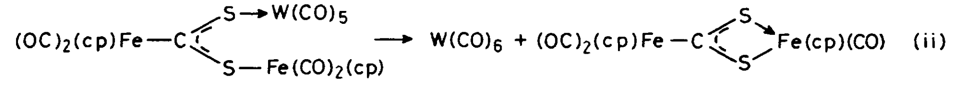
The triply bridging mode of CS_2, confirmed by the crystal-structure determination of $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2W(CO)_5]$ (3c), was first established by i.r. spectroscopy. The assignment was based primarily upon the number and relative intensities of the terminal ν(CO) absorptions which are the sum of those of the precursors (1), (2) and that attributable to the $M'(CO)_5$ or $Mn(cp)(CO)_2$ fragments. As expected (Table 1), the effect in the i.r. of adding a metal to the thione sulphur atom of derivatives (1) and (2) is to increase slightly all of their ν(CO) frequencies. These frequencies and the intensities of the ν(CO) absorptions due to the entering Lewis-acid fragments compare favourably with those in the somewhat related thioketone complexes $[M(Me_2C=S)(CO)_5]$ [9] and $M(CO)_5$ [10–11] or $Mn(cp)(CO)_2$ [11] adducts to η^2-CS_2 metal derivatives. Significantly, they are shifted towards lower wavenumbers with respect to the corresponding bands of $[M(CO)_5(PMe_3)]$ [12] and $[Mn(cp)(CO)_2(PMe_3)]$ [13] derivatives, in agreement with the good donor ability of the sulphur atom. Furthermore, examination of the CS stretching frequency region of all the μ_3-CS_2 bridged derivatives reveals a remarkably constant two-band pattern at *ca.* 950 and 770 cm^{-1} attributable to the $\nu_{asym}(CS_2)$ and $\nu_{sym}(CS_2)$ vibrations respectively.

The dithiocarboxylate nature of the μ_3-CS_2 bonding mode which delocalizes p_z electrons over the sp^2-hybridized CS_2

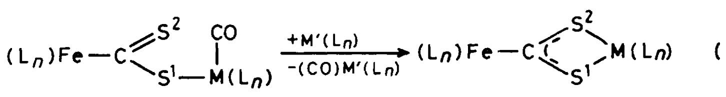
bridging system should give rise to four geometric isomers and consequently to non-equivalence of the cp n.m.r. signals, with an intensity ratio which depends on the isomer distribution. However, the room-temperature ^{1}H n.m.r. spectra in C_6D_6 show a single signal for each cyclopentadienyl ring present in the trinuclear complexes (Table 1). Since it seems unlikely that only one isomer is formed for all the μ_3-CS_2 derivatives, the observed spectra could well be due either to a fortuitous equivalence of the cp rings in the different isomers or to an equivalence on the n.m.r. time-scale arising by rapid rotation around the C$\overset{...}{-}$S bonds or inversion at the sulphur atoms. Although the reasons for this equivalence are not clear at the moment, the crystal structure of complex (3c) indicates that, at least for the $M(CO)_5$ adducts, steric hindrance forces the $W(CO)_5$ group into an *anti* position with respect to the SFe(cp)$(CO)_2$ unit. Probably, in the addition step this *anti* isomer is favoured with respect to the other possible geometric isomers, suggesting a reasonable explanation of the observed ^{1}H n.m.r. spectra.

Decomposition of μ_3-CS_2 *Complexes*.—It is known that, in its reactions with transition-metal centres, CS_2 undergoes a wide variety of cleavage and rearrangement reactions to produce fragments which are trapped by multisite bonding within the cluster framework.[14] Since this chemistry is not predictable *a priori* but must be deduced experimentally, we have studied the decomposition of the triply bridged CS_2 complexes under mild conditions in order to ascertain whether co-ordination of CS_2 to three metal atoms promotes C–S cleavage.

As mentioned above, $[(OC)_2(cp)FeC(=S)SRe(CO)_5M(CO)_5]$ (4a)—(4c) rapidly decompose in CH_2Cl_2 solvent under nitrogen. An i.r. spectrum of the decomposed sample taken after 7 h does not show the typical ν(CO) stretchings attributed to the two A_1 and E modes of the $M(CO)_5$ fragment co-ordinated through the sulphur atom, but clearly indicates the formation of $[M(CO)_6]$ and $[(OC)_2(cp)FeC(=S)SRe(CO)_4]$ (7).[5] The production of these two complexes is confirmed also by t.l.c. analysis which does not indicate the formation of other species. The series of derivatives (3a)—(3c) give similar i.r. spectra after standing for 1 d in CH_2Cl_2 solution, therefore only the decomposition of the most stable $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2W(CO)_5]$ was studied in detail by refluxing a CH_2Cl_2 solution for 4 h. Two main products have been isolated from the solution by alumina column chromatography: $[W(CO)_6]$ and $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)]$ (8), equation (ii), together with very small amounts (depending on the decomposition temperature and reaction time) of $[\{Fe(cp)(CO)_2\}_2]$.



(ii)

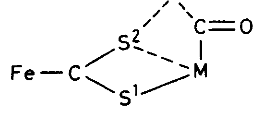


(iii)

The red air-stable complex (8) has been characterized by elemental analysis, mass, i.r., and ^{1}H n.m.r. spectra in $CDCl_3$. In the ^{1}H n.m.r. spectrum, two sharp singlets of equal intensity appear at δ 4.87 $[Fe(cp)(CO)_2]$ and 4.51 [Fe(cp)(CO)]. Equally consistent with the proposed structure is the i.r. spectrum in the carbonyl-stretching region which shows, in addition to the two ν(CO) at 2 033 and 1 986 cm^{-1} attributable to the $Fe(cp)(CO)_2$ moiety, an absorption at 1 940 cm^{-1} which falls in the region where $[Fe(cp)(S_2CSR)(CO)]$[15] and related dithiocarbamates and dithiocarboxylates absorb.[16] Furthermore, two bands are observed at 910 and 875 cm^{-1} which are due to the ν_{asym} and $\nu_{sym}(CS_2)$ stretching vibrations; this band pattern is characteristic of CS_2 bridged binuclear complexes containing a Fe–C(=S)SM unit[5] and appears also in the isoelectronic $[(OC)_2(cp)FeC(=S)SMn(cp)(NO)]$ (9), which has been prepared from $[Fe(cp)(CO)_2(CS_2)]^-$ and $[Mn(cp)(CO)_2(NO)]^+$.

Although it has been reported[4] that complex (8) is not produced from $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2]$ by thermal or photolytic means, we have found its formation in 17% yield from photolysis of (1) in thf solvent and in trace amount, as indicated by t.l.c. analysis, upon refluxing for 24 h a CH_2Cl_2 solution of the iron dithioester complex (1). Higher decomposition temperatures, refluxing n-octane, or at 120 °C in the solid state afford CS_2 and $[\{Fe(cp)(CO)_2\}_2]$.

These findings are in agreement with the properties of the other two known metallodithioester–metal complexes $[(OC)_2(cp)FeC(=S)SRe(CO)_5]$[5] and $[Ph_3SnC(=S)SRe(CO)_5]$[17] which can be obtained only if the conditions are sufficiently mild to avoid formation of the chelated complexes. The ease with which type (ii) reactions occur in these and in all the related derivatives listed in Scheme 1, in comparison with the corresponding chelation processes, clearly suggests that the addition of the molecular Lewis acids $M'(L_n)$ substantially increases the rate of the kinetically controlled metallodithiocarboxylate formation. Although a mechanistic investigation was not conducted, type (1) or (2) complexes may be considered as stable intermediates of reaction (iii) which, owing to the dipolar nature of the $\overset{...}{-}S^2 \longrightarrow M'(L_n)$ bond and the steric strain around the $M(CO)_5$ fragment (see next section), enhances the sulphur–metal and carbonyl carbon–metal interactions to form an intermediate (I) containing two four-membered rings and which may account for the formation of the observed products.



(I)

The Crystal and Molecular Structure of $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2W(CO)_5]$.—The crystal contains discrete molecules showing normal intermolecular contacts. The trimetallic complex consists of three organometallic fragments, two $Fe(\eta^5$-$C_5H_5)(CO)_2$ and one $W(CO)_5$, linked through a CS_2 molecule acting as a tridentate ligand (Figure). To our knowledge this is the first structural report in which carbon disulphide displays such a co-ordination geometry. The iron atoms in the two $Fe(\eta^5$-$C_5H_5)(CO)_2$ fragments possess 17 valence electrons and therefore they receive one electron from

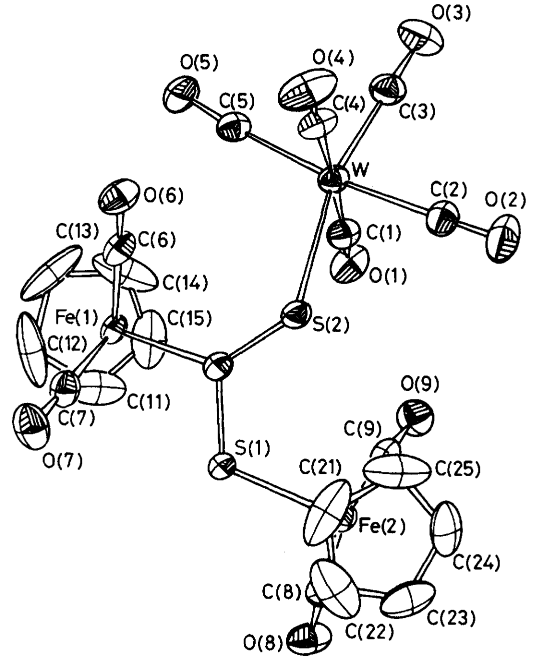


Figure. ORTEP drawing of the molecule showing 30% thermal ellipsoids; the hydrogen atoms of the C_5H_5 ligands are omitted

the co-ordinated carbon and sulphur atoms of the CS_2 ligand. The $W(CO)_5$ fragment, on the other hand, accepts two electrons from the second sulphur atom in order to fill up its valence shell. The CS_2 ligand therefore acts as a tridentate four-electron donor and should be described as a dithiocarboxylate fragment.

The geometry of the CS_2 ligand, as usual when co-ordinated, is far from that of the gaseous molecule. The carbon atom is trigonally hybridized [S–C–S 119.2(2)°] and the unhybridized p_z orbital strongly interacts with the analogous p_z orbitals on the sulphur atoms giving a system of orbitals delocalized over three atoms. In fact an sp^2 hybridization of the donor sulphur orbitals can be deduced from the angles Fe(2)–S(1)–C [115.8(2)°] and W–S(2)–C [125.9(2)°]. The C–S distances show double-bond character (average 1.69 Å), as one can infer from a comparison with the extreme values found in the molecules CS_2 (1.56 Å)[18] and Me_2S (1.81 Å).[19] In spite of the new kind of co-ordination the bond distances are in the range of those found in a variety of CS_2 complexes. The slight but significant difference in the two C–S distances [C–S(1) 1.715(4), C–S(2) 1.670(5) Å] indicates the non-equivalence of the two sulphur-metal interactions. Significantly, the C–S(2) distance, the sulphur atom of which acts as a two-electron donor to the $W(CO)_5$ group, is shorter than C–S(1), where the sulphur donates only one electron to a fragment $Fe(\eta^5\text{-}C_5H_5)(CO)_2$. As a consequence more positive charge is localized on S(2) which results in a shrinkage of its orbitals.

Looking at the overall molecular geometry one should note that the molecule is asymmetrical but, since the crystal space group is centric, equal amounts of enantiomeric molecules are present. The actual conformation around the sulphur atoms is not the only one possible, their being two donating sites at each trigonally hybridized sulphur atom. Among the four geometric isomers the one minimizing the intramolecular contacts is adopted, as one can infer from the propeller-like arrangement of the organometallic fragments at the sulphur atoms and from the fact that the fragment facing the carbon-bonded Fe(1) is the one with longer sulphur-metal distance [S(2)–W 2.563(1) and S(1)–Fe(2) 2.273(1) Å]. In addition, the $W(CO)_5$ fragment probably has a more appropriate shape and allows better contacts with the ligands bonded to Fe(1). Notwithstanding this the interligand contacts would still be too tight and in order to alleviate them the following main deformations take place: (i) a significant tilting of the whole $W(CO)_5$ group [*trans* angle C(3)–W–S(2) 165.9(2)°]; (*ii*) an opening of the W–S(2)–C angle [125.9(2)°]; (*iii*) an opening of the S(2)–C–Fe(1) angle [128.9(2)°]; (*iv*) a displacement of the tungsten atom out of the S(1)–C–S(2) plane (1.06 Å downward with reference to the Figure). Such a situation is expected to induce an enhanced chemical reactivity in this region of the molecule (see above).

The two $Fe(\eta^5\text{-}C_5H_5)(CO)_2$ fragments show the same conformation but opposite orientation with respect to the CS_2 plane. The bond parameters in these groups are normal and strictly comparable. No significant differences arise from the co-ordination through the carbon and sulphur atoms of the CS_2 molecule, therefore there is no evidence of appreciable difference between the basicity of the carbon and sulphur atoms in the present system. The Fe(1)–C(carbon disulphide) bond distance [1.975(4) Å] can be compared to the average Fe–C (carbonyl) value (1.77 Å) in order to rule out any significant π interaction.

The metal-carbonyl interactions show comparable C–O distances as far as the iron-bonded and the equatorial ligands in $W(CO)_5$ are concerned, indicating that the π bonding in the CO groups *trans* to themselves and the cyclopentadienyl ligand is substantially equivalent. More singular is the situation of C(3)–O(3) bonded to the tungsten *trans* to the sulphur atom. A comparison of the bond values in this apical and in the equatorial ligands shows shorter W–C and longer C–O values, respectively (W–C 1.97 and 2.04; C–O 1.16 and 1.13 Å), confirming the good donor ability of the sulphur ligand. No comment is made on the cyclopentadienyl ligands because of their high thermal motion.

Conclusions

Stepwise metallation of the σ-CS_2 metal adduct $[Fe(cp)(CO)_2(CS_2)]^-$ described herein is of interest for several reasons: (*i*) it provides a stable novel type of co-ordination for carbon disulphide in CS_2-containing complexes; (*ii*) in principle it has synthetic interest, indicating an easy way to obtain a large variety of neutral dithiocarboxylato- or cationic dithiocarbene[20] triply bridged CS_2 complexes; (*iii*) it may suggest that activation of the CS_2 molecule by metal atoms, which promotes many examples of carbon–sulphur cleavage or carbon disulphide rearrangement, does not occur through a trimetallic interaction MC(=S)SM′M″ which favours decarbonylation rather than desulphurization reactions.

Experimental

General.—All reactions were performed under nitrogen using standard inert-atmosphere techniques. Infrared spectra were recorded on Perkin-Elmer 257 or 225 spectrometers, ^1H n.m.r. spectra on a Varian XL 100 spectrometer using $SiMe_4$ as internal standard, and mass spectra on a JEOL JMS-D 100 spectrometer working at 75 eV (*ca.* 1.20×10^{-17} J). Microanalyses were determined by Schwarztkopfe Microanalytical Laboratorium (Bonn, Germany). The compounds $[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2]$ (1) and $[(OC)_2(cp)FeC(=S)SRe(CO)_5]$ (2) were prepared as in refs. 4 and 5. Spectroscopic data are given in Table 1.

Preparation of the Complexes.—$[(OC)_2(cp)FeC(=S)SFe(cp)(CO)_2M'(CO)_5]$ (3a)—(3c) [M′ = Cr (a), Mo (b), *or* W (c)]. To a solution of [M′(CO)$_5$(thf)], prepared by irradiation of [M′(CO)$_6$] (0.50 mmol) in freshly distilled thf (20 cm^3), was added [(OC)$_2$(cp)FeC(=S)SFe(cp)(CO)$_2$] (1) (0.129 g, 0.30 mmol). The deep red solution was stirred for 120 min at room temperature; the solvent was then removed under vacuum and the residue washed with light petroleum (b.p. 40—70 °C, 50 cm^3). The resulting solid was dried under vacuum and the red complexes (3a)—(3c) were crystallized from CH$_2$Cl$_2$–hexane mixture at −20 °C. (3a): yield 58% (0.108 g, 0.17 mmol); m.p. 122—123 °C (decomp.) (Found: C, 38.45; H, 1.60; O, 23.4; S, 10.2. Calc. for C$_{20}$H$_{10}$CrFe$_2$O$_9$S$_2$: C, 38.6; H, 1.60; O, 23.15; S, 10.3%). (3b): yield 40% (0.080 g, 0.12 mmol); m.p. 105—106 °C (decomp.) (Found: C, 36.0; H, 1.50; S, 9.75. Calc. for C$_{20}$H$_{10}$Fe$_2$MoO$_9$S$_2$: C, 36.05; H, 1.50; S, 9.65%). (3c): yield 75% (0.170 g, 0.22 mmol); m.p. 141—142 °C (decomp.) (Found: C, 31.65; H, 1.40; S, 8.50. Calc. for C$_{20}$H$_{10}$Fe$_2$O$_9$S$_2$W: C, 31.85; H, 1.35; S, 8.50%).

[(OC)$_2$(cp)FeC(=S)SFe(cp)(CO)$_2$Mn(cp)(CO)$_2$] (5). To a solution of [Mn(cp)(CO)$_2$(thf)] prepared by irradiation of [Mn(cp)(CO)$_3$] (0.204 g, 1 mmol) in freshly distilled thf (20 cm^3), was added complex (1) (0.258 g, 0.6 mmol). The solution was stirred for 3 h at room temperature. The solvent was then removed under vacuum and the residue washed with light petroleum (60 cm^3). The resulting solid was dried overnight under vacuum and the red-brown title complex was crystallized from CH$_2$Cl$_2$–hexane at −20 °C. Yield 38% (0.138 g, 0.23 mmol); m.p. 114—115 °C (decomp.) (Found: C, 43.65; H, 2.55; S, 10.45. Calc. for C$_{22}$H$_{15}$Fe$_2$MnO$_6$S$_2$: C, 43.6; H, 2.50; S, 10.6%).

[(OC)$_2$(cp)FeC(=S)SRe(CO)$_5$M′(CO)$_5$] (4a)—(4c) [M′ = Cr (a), Mo (b), *or* W (c)]. These complexes were prepared by a route analogous to that used for (3a)—(3c) starting with a solution of [M′(CO)$_5$(thf)] (0.5 mmol) in thf (20 cm^3) and [(OC)$_2$(cp)FeC(=S)SRe(CO)$_5$] (2) (0.180 g, 0.31 mmol). This solution was evaporated to dryness after being stirred for 30 min. The resulting residue was washed with three 25-cm^3 portions of light petroleum and dried under vacuum overnight. The orange complexes (4a)—(4c) were crystallized from a CH$_2$Cl$_2$–hexane mixture at −20 °C. (4a): yield 43% (0.103 g, 0.13 mmol); m.p. 114—115 °C (decomp.) (Found: C, 27.85; H, 0.75; S, 8.40. Calc. for C$_{18}$H$_5$CrFeO$_{12}$ReS$_2$: C, 28.0; H, 0.65; S, 8.30%). (4b): yield 32% (0.081 g, 0.10 mmol); m.p. 109—110 °C (decomp.) (Found: C, 26.45; H, 0.65; S, 8.15. Calc. for C$_{18}$H$_5$FeMoO$_{12}$ReS$_2$: C, 26.5; H, 0.60; S, 7.85%). (4c): yield 65% (0.182 g, 0.20 mmol); m.p. 129—130 °C (decomp.) (Found: C, 23.65; H, 0.65; S, 7.20. Calc. for C$_{18}$H$_5$FeO$_{12}$ReS$_2$W: C, 23.95; H, 0.55; S, 7.10%).

[(OC)$_2$(cp)FeC(=S)SRe(CO)$_5$Mn(cp)(CO)$_2$] (6). This red-brown complex was prepared and crystallized as described above for the analogous derivative (5). It decomposes rapidly in solutions of chlorinated solvents to give [Mn(cp)(CO)$_3$] and [(OC)$_2$(cp)FeC(=S)SRe(CO)$_4$]; this accounts for the low yield (*ca.* 18%) with which it is obtained; m.p. 108—109 °C (decomp.) (Found: C, 31.5; H, 1.55; S, 8.30. Calc. for C$_{20}$H$_{10}$FeMnO$_9$ReS$_2$: C, 31.8; H, 1.35; S, 8.50%).

[(OC)$_2$(cp)FeC(=S)SFe(cp)(CO)] (8). A thf solution containing complex (1) (0.400 g, 0.93 mmol) was irradiated under nitrogen with a Hanovia ultraviolet lamp for 2 h. The resulting solution was evaporated to dryness under vacuum and the residue chromatographed on an alumina column. Elution with light petroleum–CH$_2$Cl$_2$ (1 : 1) gave first a red fraction which was dried under vacuum for 12 h. The red solid was dissolved on CH$_2$Cl$_2$ and filtered through alumina. Crystallization from CH$_2$Cl$_2$–hexane at −20 °C gave red needles (0.064 g, 0.16 mmol, 17%) of the title complex (8); m.p. 114—115 °C (decomp.) (Found: C, 41.9; H, 2.60; S, 15.85. Calc. for C$_{14}$H$_{10}$Fe$_2$O$_3$S$_2$: C, 41.8; H, 2.50; S, 15.95%). Mass spectrum: *m/e* 402 (M^+); 374, 346, and 318 (base peak) ($M - n$CO, where n = 1—3).

[(OC)$_2$(cp)FeC(=S)SMn(cp)(NO)] (9). A solution of [Fe(cp)(CO)$_2$]$^-$ (ref. 3) (*ca.* 1.6 mmol) in thf (10 cm^3) was added with a syringe to CS$_2$ (1 cm^3) at −78 °C. After 30 s [Mn(cp)(CO)$_2$(NO)]PF$_6$[21] (0.440 g, 1.25 mmol) dissolved in thf (10 cm^3) was added and stirring was continued for 30 min. The reaction mixture was then allowed to warm to room temperature, the solvent evaporated, and the residue chromatographed on an alumina column. Elution with light petroleum–CH$_2$Cl$_2$ (2 : 1) gave first a fraction which contained very small amounts of complex (8), and a second and a third fraction which contained [(OC)$_2$(cp)FeC(=S)SFe(cp)(CO)$_2$]. The yellow residue obtained from the second fraction was crystallized at −20 °C from light petroleum–CH$_2$Cl$_2$ and gave microcrystalline (9) (0.207 g, 0.51 mmol, 41%); m.p. 96—98 °C (Found: C, 38.6; H, 2.65; S, 15.85. Calc. for C$_{13}$H$_{10}$FeMnNO$_3$S$_2$: C, 38.75; H, 2.50; S, 15.9%). Mass spectrum: *m/e* 403 (M^+), 373 (M^+ − NO, base peak), 347 (M^+ − 2CO), and 317 (M^+ − 2CO − NO).

Decomposition of [(OC)$_2$(cp)FeC(=S)SFe(cp)(CO)$_2$W(CO)$_5$] (3c).—A solution of complex (3c) (0.200 g, 0.26 mmol) in CH$_2$Cl$_2$ (20 cm^3) was refluxed for 4 h. The solvent was evaporated to dryness under vacuum and the residue chromatographed on an alumina column. Elution with light petroleum–CH$_2$Cl$_2$ (4 : 1) gave three fractions in the following sequence: (*a*) W(CO)$_6$, (*b*) complex (8) (0.075 g, 0.18 mmol, 70%), and (*c*) [{Fe(cp)(CO)$_2$}$_2$]. The nature of these compounds was established by comparison of the i.r. and ^{1}H n.m.r. spectra with those of authentic samples.

X-*Ray Crystal-structure Analysis*.—*Crystal data*. (3c), C$_{20}$H$_{10}$Fe$_2$O$_9$S$_2$W, M = 753.95, Triclinic, space group $P\bar{1}$, a = 6.647(1), b = 12.145(2), c = 14.795(2) Å, α = 82.33(1), β = 85.73(1), γ = 79.73(1)°, U = 1 163.16 Å^3, Z = 2, D_c = 2.15 g cm^{-3}, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 64.92 cm^{-1}. A single crystal of dimensions *ca.* 0.20 × 0.11 × 0.12 mm was mounted on an Enraf-Nonius CAD4 diffractometer. The lattice constants were obtained by least-squares refinement based on precise 2θ measurements of 25 independent reflections.

Collection and reduction of X-*ray intensity data*. The diffraction intensities were collected with graphite-monochromated Mo-K_α radiation. All the independent data (5 094 reflections) within a 2θ sphere of 54° were measured by using the ω-scan technique, with scan range $\Delta\omega = 1.1 + 0.35\tan\theta$ and background counted for a half of the peak-scanning time. Each reflection was prescanned at high speed (20° min^{-1}). If the intensity was found to be either very strong [$I > 20\sigma(I)$] or very weak [$I < 2\sigma(I)$] the measurement was not repeated. Strong reflections were accepted as measured, weak ones were rejected. In all other cases the scan was repeated at a speed, determined by the control program, that would allow approach to the desired precision [I *ca.* $25\sigma(I)$], with the limiting factor being a maximum time of 35 s. The intensities of three standard reflections were measured every 60 min and no significant crystal decay was observed. The crystal orientation was also checked every 200 reflections. The measured intensities were corrected for Lorentz and polarization effects, and an experimental correction for absorption was applied. 3 487 Intensities with $I > 3\sigma(I)$ were retained for the structure solution and refinement.

Solution and refinement of the structure. All the computations

Table 2. Final positional parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.088 23(3)	0.116 16(2)	0.164 75(1)	C(3)	0.224 6(8)	0.005 2(4)	0.084 8(4)
Fe(1)	0.083 6(1)	0.254 43(5)	0.436 60(4)	C(4)	−0.159 9(9)	0.036 1(4)	0.191 1(4)
Fe(2)	−0.195 8(1)	0.594 01(5)	0.202 85(4)	C(5)	0.217 6(8)	0.008 2(4)	0.270 3(4)
S(1)	−0.086 6(2)	0.482 8(1)	0.331 87(8)	C(6)	−0.049 8(7)	0.143 0(4)	0.426 3(3)
S(2)	−0.099 2(2)	0.292 7(1)	0.231 98(9)	C(7)	−0.120 5(8)	0.320 0(5)	0.506 5(4)
O(1)	0.469 2(6)	0.243 0(3)	0.133 9(3)	C(8)	−0.053 4(8)	0.695 2(4)	0.228 1(4)
O(2)	−0.108 8(8)	0.256 5(4)	−0.012 9(3)	C(9)	0.006 4(7)	0.524 1(4)	0.135 4(3)
O(3)	0.307 4(8)	−0.058 1(4)	0.036 2(3)	C(11)	0.324 3(10)	0.334 9(6)	0.457 1(6)
O(4)	−0.291 5(6)	−0.011 5(4)	0.206 5(4)	C(12)	0.298 2(10)	0.257 0(10)	0.529 4(4)
O(5)	0.289 5(7)	−0.058 2(3)	0.325 4(3)	C(13)	0.339 6(10)	0.154 3(6)	0.497 0(6)
O(6)	−0.138 4(6)	0.072 2(3)	0.423 3(3)	C(14)	0.380 7(9)	0.177 1(6)	0.407 4(6)
O(7)	−0.247 6(7)	0.359 4(4)	0.552 6(3)	C(15)	0.371 5(9)	0.284 1(8)	0.386 2(5)
O(8)	0.030 6(7)	0.763 2(3)	0.243 9(3)	C(21)	−0.494 9(10)	0.571 1(7)	0.236 2(6)
O(9)	0.137 8(6)	0.484 3(3)	0.089 5(3)	C(22)	−0.485 5(10)	0.678 3(8)	0.234 1(5)
C	−0.037 4(7)	0.340 6(4)	0.325 1(3)	C(23)	−0.427 9(10)	0.719 1(6)	0.150 7(6)
C(1)	0.333 7(7)	0.197 3(4)	0.145 1(4)	C(24)	−0.394 0(9)	0.635 8(7)	0.097 8(4)
C(2)	−0.041 1(8)	0.208 2(4)	0.050 7(4)	C(25)	−0.434 4(9)	0.538 3(6)	0.150 9(6)

Table 3. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

W-S(2)	2.563(1)	C(6)-O(6)	1.132(6)	Fe(1)-C(13)	2.091(6)	Fe(2)-C(25)	2.066(6)
W-C(1)	2.035(5)	Fe(1)-C(7)	1.781(6)	Fe(1)-C(14)	2.071(7)	C(21)-C(22)	1.31(1)
C(1)-O(1)	1.121(6)	C(7)-O(7)	1.125(6)	Fe(1)-C(15)	2.076(6)	C(22)-C(23)	1.32(1)
W-C(2)	2.050(6)	Fe(2)-S(1)	2.273(1)	C(11)-C(12)	1.35(1)	C(23)-C(24)	1.34(1)
C(2)-O(2)	1.131(6)	Fe(2)-C(8)	1.771(6)	C(12)-C(13)	1.37(1)	C(24)-C(25)	1.39(1)
W-C(3)	1.967(6)	C(8)-O(8)	1.133(6)	C(13)-C(14)	1.34(1)	C(25)-C(21)	1.38(1)
C(3)-O(3)	1.160(6)	Fe(2)-C(9)	1.773(5)	C(14)-C(15)	1.29(1)	Fe(1) · · · S(1)	3.06(1)
W-C(4)	2.047(6)	C(9)-O(9)	1.143(6)	C(15)-C(11)	1.28(1)	Fe(1) · · · S(2)	3.29(1)
C(4)-O(4)	1.126(6)	S(1)-C	1.715(4)	Fe(2)-C(21)	2.071(7)	Fe(2) · · · S(2)	3.57(1)
W-C(5)	2.036(6)	S(2)-C	1.670(5)	Fe(2)-C(22)	2.064(7)	Fe(2) · · · C	3.39(1)
C(5)-O(5)	1.136(6)	Fe(1)-C(11)	2.078(7)	Fe(2)-C(23)	2.077(6)	C(5) · · · H(14)	2.66(1)
Fe(1)-C	1.975(4)	Fe(1)-C(12)	2.058(7)	Fe(2)-C(24)	2.065(6)	O(5) · · · H(14)	2.64(1)
Fe(1)-C(6)	1.773(5)						

S(2)-W-C(1)	85.7(1)	C(5)-W-C(1)	92.0(2)	C(8)-Fe(2)-C(9)	94.2(2)
S(2)-W-C(2)	79.4(2)	W-S(2)-C	125.9(2)	W-C(1)-O(1)	179.5(5)
S(2)-W-C(4)	92.5(2)	Fe(2)-S(1)-C	115.8(2)	W-C(2)-O(2)	178.2(6)
S(2)-W-C(5)	106.9(2)	S(1)-C-S(2)	119.2(2)	W-C(3)-O(3)	178.2(5)
S(2)-W-C(3)	165.9(2)	S(2)-C-Fe(1)	128.9(2)	W-C(4)-O(4)	177.5(5)
C(3)-W-C(1)	90.1(2)	S(1)-C-Fe(1)	111.9(2)	W-C(5)-O(5)	175.0(5)
C(3)-W-C(2)	87.4(2)	C-Fe(1)-C(7)	91.2(2)	Fe(1)-C(6)-O(6)	177.2(5)
C(3)-W-C(4)	92.2(2)	C-Fe(1)-C(6)	90.5(2)	Fe(1)-C(7)-O(7)	178.1(5)
C(3)-W-C(5)	86.6(2)	C(6)-Fe(1)-C(7)	91.6(2)	Fe(2)-C(8)-O(8)	177.2(5)
C(1)-W-C(2)	91.2(2)	S(1)-Fe(2)-C(9)	91.6(2)	Fe(2)-C(9)-O(9)	176.5(4)
C(2)-W-C(4)	90.6(2)	S(1)-Fe(2)-C(8)	89.0(2)		
C(4)-W-C(5)	86.4(2)				

were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP package of crystallographic programs. A Patterson map revealed the positions of the metal atoms and subsequent structure factors and electron-density maps revealed the positions of all the other atoms, except the hydrogens. Positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations. A difference-Fourier map, computed at this stage, revealed most of the hydrogen atoms of the cyclopentadienyl ligands; these atoms were placed in calculated positions and not refined. The final cycles of refinement were computed with the weighting factor $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2$, with F_o derived from counting statistics. The resulting error of an observation of unit weight was 1.34. The final conventional residual index was $R = \Sigma|F_o - |F_c||/\Sigma|F_c| = 0.024$ and $R' = 0.031$. A difference-Fourier map, computed with the final set of structure parameters, showed residual peaks of *ca.* 0.5 e Å^{-3} in the vicinity of the cyclopentadienyl ligands.

Fractional co-ordinates are reported in Table 2, bond distances and angles in Table 3.

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